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Synthesis of magnetic functionalized MWCNT nanocomposite through surface RAFT co-polymerization of acrylic acid and N-isopropyl acrylamide for removal of cationic dyes from aqueous solutions

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ABSTRACT

In this study, magnetic multi-walled carbon nanotube (MMWCNT) composites were prepared via surface reversible addition fragmentation chain transfer (RAFT) co-polymerization of acrylic acid (AA) and N-isopropyl acrylamide (NIPAM) in the presence of Fe_3O_4 nanoparticles. First, a novel RAFT agent (RA) was prepared and then immobilized onto the surface of MWCNT to fabricate RA-g-MWCNT. Then, Fe_3O_4 nanoparticles were attached onto the surface of RA-g-MWCNT. Finally, RAFT co-polymerization of AA and NIPAM monomers was carried out via Fe_3O_4-g-RA-g-MWCNT RAFT agent. The structure and morphology of the prepared polymer-coated MWCNT was examined by FTIR, SEM, TEM, XRD, VSM, and TGA. The adsorption behaviours of the cationic dyes were studied. The equilibrium isotherm and kinetics of cationic dyes were investigated. Thermodynamics investigations also depicted that the adsorptions of cationic dyes were spontaneous and endothermic in nature. The synthesized dye adsorbent with high adsorption capacities, reusability, and easy recovery makes it as a good candidate for wastewater treatment.

1. Introduction

Magnetic carbon nanotubes (CNTs) in the form of single- (SWCNT) and multi-walled (MWCNT) hybrid materials have attracted considerable attention from scientific communities owing to their promising applications in a variety of technical fields, such as medical and biosensors (Freedman et al., 2007; Singhal et al., 2011; Syljukic et al., 2006; Olivé-Monllau et al., 2013; Qu et al., 2007), environmental (Chen et al., 2009; Gupta et al., 2011; Ma et al., 2013; Hu et al., 2010), magnetic data storage (Cava et al., 2014), catalysis (Goh et al., 2012; Zuo et al., 2009), and electronic devices (Samouhos and McKinley, 2007). The utilization of the CNT can be adjusted when using magnetic CNT composites because the CNT can be aligned by applying an external magnetic field (Zhang et al., 1999; Korneva et al., 2008; Kornev et al., 2008).

By chemically modifying CNTs, we can improve their properties to meet the requirements of a given application. Hence, it is necessary to decorate CNTs surfaces with suitable functional groups and/or nanoparticles to merge them into chosen structures.

CNTs can be decorated with magnetic nanoparticles by two possible approaches: (i) grafting Fe_3O_4 nanoparticles on their surface or (ii) placing Fe_3O_4 nanoparticles inside their channels. Surface modification of CNTs is performed in two ways: by covalent attachment of chemical groups from an appropriate compound and/or by noncovalent adsorption (Tasis et al., 2006). To include nanoparticles within CNTs structure, two ways are often used with different numbers of preparation steps (Xu et al., 2004, 2009; Huo et al., 2004): (i) in one-step process, metal oxide nanoparticles grow with the evolution of the CNT skeleton; (ii) in two-step process, for the formation of metal oxide nanoparticles, the end of CNTs are cut and filled with liquid containing precursors.

Covalent polymer chains attached to the surfaces of SWCNTs and MWCNTs are the mostly considered components that not only lead to a new surface structure of CNTs but also provide an opportunity to have variable chemical functionalities and therefore different application areas (Wang et al., 2004; Liu, 2005; Tasis et al., 2006; Sun et al., 2002; Hill et al., 2002). To acquire such structure, polymer grafting is carried out by three methods: “grafting from”, “grafting through”, and “grafting to”. In the “Grafting from” and “grafting through” reactions, the polymerization was based in the presence of a substrate; however, “grafting onto” uses polymeric chains. Among these three methods, “grafting from” is the top choice due to the maximum grafting density

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that can be achieved thanks to the lower steric hindrance in the propagation step (Roghani-Mamaqani et al., 2012). To perform a "grafting from", controlled radical polymerization (CRP) techniques are mainly employed (Hojjati and Charpentier, 2008; Samakande et al., 2008). Surface reversible addition fragmentation chain transfer (RAFT) is the most effective polymerization technique of the CRP methods, due to the resistance to environmental conditions and reactivity toward various types of monomers (Lowe and McCormick, 2007).

Dyes are produced in large amounts from industries such as textiles, printing, cosmetics, and therefore, they are released into the environment (Zhou et al., 2014; Mittal et al., 2015). Thus, the removal of dyes as major water pollutants from wastewater has been given much attention in the last few years (Oladipo et al., 2014; Deniz, 2013). There are various promising physico-chemical techniques for the adsorption of dyes from wastewaters such as: chemical coagulation/flocculation, oxidation, nano-filtration, chemical precipitation, and ion exchange (Cao et al., 2012; Morshedi et al., 2013; Majewska-Nowak et al., 2006). However, these treatment processes have serious limitations such as high cost and generation of toxic sludge. In addition, new treatment methods and efficient dye adsorbents still need with faster adsorption kinetics and higher capacity. On the other hand, adsorption is the most economical and effective method for the dyes removal mainly due to its cheapness, effectiveness and easy operation (Chatterjee et al., 2011; Wang et al., 2016; Mahdavinia et al., 2014).

Recently, using of nanomaterials in wastewater applications has received wide attention. In this regard, many nanomaterials such as CNTs, nanoclays, nanofibers, and polymer-based nanocomposites have been used to develop novel dye adsorbents and exhibited exceptional performance (Tan et al., 2015). The large specific surface area, good mechanical stability, high selectivity, easily preparation method, and more active sites offer nanomaterials as excellent materials in treatment of dye-contaminated wastewater (Chen, 2011). Thus, nanomaterials can be used as economical materials for the revolution of wastewater treatment applications.

Owing to their unique properties, MWCNTs as carbonaceous nanomaterials have been extensively applied for wastewater treatment. MWCNTs are promising adsorbents for treating effluents due to the high specific surface area, large pore volume, and more sorption sites. Meanwhile, chemical modification of MWCNTs improves the dye adsorption behaviour. In fact, more studies indicated that the functionalized MWCNTs exhibited higher dye adsorption capacity and faster adsorption kinetics than the pristine ones.

However, only a few studies have been reported on the using of MWCNTs for dye adsorption from aqueous solution (Sui et al., 2012; Bahgat et al., 2011; Ghaedi et al., 2011a, 2011b; Machado et al., 2011). Therefore, considering the aforementioned advantages of RAFT polymerization method and MWCNT properties, we reported here a facile method to fabricate magnetic MWCNTs nanocomposites. Surface of MWCNT was decorated with esterification reaction of Fe_3O_4 nanoparticles using RAFT method. Then, acrylic chains were propagated from the edge-anchored magnetic MWCNT-RAFT agent. The main goal of the present study was to investigate the potentiality of using modified MWCNT as an effective adsorbent for the removal of various cationic dyes from aqueous solutions. The kinetics, thermodynamics and isotherms of the as-prepared adsorbents were also discussed in detail.

2. Experimental

2.1. Materials

Acrylic acid (AA, Aldrich, 99%), N-isopropyl acrylamide (NIPAM, Aldrich, 99%), OH functionalized short MWCNTs (> 95%, OD: 5–15 nm; US Research Nanomaterials, Inc.), 2,2′-tetrabutylammonium hydrogen sulphate (Merck), sulfuric acid (H_2SO_4, Merck), N,N′-dicyclohexylcarbodiimide (DCC, Aldrich, 99%), 4-dimethylaminopyrdine (DMAP, Aldrich, 99%), carbon disulfide (Sigma-Aldrich, > 99%), sodium hydroxide (NaOH, Merck), acetone (Merck), N,N′-dimethylformamide (DMF, Merck), and chloroform (Merck) were used as received. Azoisobutyronitrile (AIBN, Aldrich, 98%) was recrystallized twice from methanol. The cationic dyes methylene blue (MB), crystal violet (CV), and Rhodamine B (RhB) were obtained from Sigma-Aldrich and used as received. The molecular structure and identification information of the three cationic dyes are depicted in Table S1.

2.2. Synthesis Fe_3O_4 magnetic nanoparticles

The synthesis of Fe_3O_4 magnetic nanoparticles was conducted by co-precipitation method (Liu, 2004). Briefly, the soluble ferric chloride and ferrous chloride with a molar ratio of 3:2 in 80 mL of deionized water were mixed under vigorous stirring with protection of nitrogen (An et al., 2004). Then aqueous ammonium hydroxide was added gradually into the mixture until the pH value was titrated to 11.0 (Wei et al., 2012; Zhang et al., 2006; Jiang et al., 2004). The solution became black due to the formation of iron oxide magnetic nanoparticles. The sample was continuously reacted in oil bath at 65 °C for 60 min under vigorous stirring. The as-prepared nanoparticles were finally removed from the solution by a strong magnet and then washed with distilled water. The precipitated magnetite was black in colour. The powder was dried in a hot air oven at 100 °C overnight.

2.3. Synthesis of RAFT agent

In this study, S,S′-bis(α,α′-dimethyl-α″-acetic acid)-trithiocarbonate (BDATC) was chosen as the chain transfer agent (CTA). The trithiocarbonate RAFT agent was synthesized by using the methods reported previously (Lai et al., 2002; Tominey et al., 2010). Briefly, carbon disulfide (10.87 mL, 0.18 mol), chloroform (36.25 mL, 0.045 mol), acetone (33.1 mL, 0.045 mol), and tetrabutylammonium hydrogen sulphate (1.21 g, 3.55 mmol) were mixed with 60 mL of toluene in a 500 mL three-necked round-bottom flask equipped with a mechanical stirrer and an additional funnel under nitrogen. Sodium hydroxide (100.8 g, 1.26 mol, 50%) was added dropwise over 90 min to keep the temperature below 25 °C and the reaction was stirred for 24 h. Then, 300 mL of distilled water was added to separate the mixture into two layers. The organic layer was discarded, and the aqueous layer was acidified with 50 mL of concentrated HCl to precipitate the product as a yellow solid product. Finally, 6.42 g of RAFT agent product was collected after filtration and then dried in air (21.75% yield).

2.4. Synthesis of MWCNT-RAFT agent

MWCNT-OH (0.50 g) was dissolved in 50 mL of DMF in a 100 mL flask, and ultrasonically dispersed for 15 min. Then, RA (BDATC, 1 g, 3.6 mmol) was added and continuously stirred for its dissolution. Afterward, DCC (6 g, 31.3 mmol) and DMAP (0.45 g, 3.69 mmol) were added to the solution, and the mixture was stirred at 25 °C for 24 h. The produced solid was then filtered using a 0.2 μm PTFE filter and washed with THF solution. The product was first dispersed in H_2O (200 mL) and separated by centrifugation. The obtained sample was dried at vacuum oven at 40 °C to give 0.43 g of MWCNT-RAFT agent. Scheme 1 shows the preparation of MWCNT-RAFT agent.

2.5. Synthesis of Fe_3O_4-g-RA-g-MWCNT

Fe_3O_4 nanoparticles were attached onto the surface of RA-g-MWCNT through an esterification reaction between the hydroxyl groups of nanoparticles and the carboxyl groups of RA to produce Fe_3O_4-g-RA-g-MWCNT. RA-g-MWCNT (0.50 g) was dissolved in 80 mL of DMF in a 100 mL flask and ultrasonically dispersed for 20 min, and then Fe_3O_4 (0.7 g, 3 mmol) was added and ultrasonically dispersed. Afterward, DCC (6 g, 31.3 mmol) and DMAP (0.45 g, 3.69 mmol) were added to the solution. The mixture was stirred at 25 °C for 24 h. The